Gas-surface chemical reactions at high collision energies?

Michael J. Gordon,[†] *Xiangdong Qin,*[‡] *Alex Kutana,*[‡] *Konstantinos P. Giapis*[‡]

[†]Department of Chemical Engineering, University of California – Santa Barbara, Santa Barbara, CA 93106-5080.

[‡] Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, CA 91125.

Supplementary Information

Simulation of scattering of F on an AgF surface

1. Surface structure

For the fluorinated Ag surface, we used the geometric parameters of Ag (111) with 0.111 ML F, as obtained from density functional theory (DFT) calculations[1]. Fluorine atoms occupy 3-fold fcc sites at a normal distance of 1.650 Å from the average surface plane, as listed in Table 6 of ref. [1]. Table 8 of ref. [1] gives the nearest neighbor F-Ag distance of 2.348 Å, indicating very little change of the Ag-Ag distance in the top Ag layer with respect to the bulk value. The actual F coverage used in the scattering simulation was increased to 1 ML to improve the statistics. The 3x3 supercell of the Ag(111) surface with two monolayers of silver atoms was used to represent the substrate, with periodic boundary conditions applied only in the lateral dimensions.

2. Interatomic potentials

A hybrid Morse-Molière pair potential $U_{tot}(r)$ was employed in the scattering simulations:

$$U_{tot}(r) = f_{c1}(r)U_{core}(r) + \left(1 - f_{c1}(r)\right) f_{c2}(r)U_{reac}(r) \tag{1}$$

where $U_{core}(r)$ is the term responsible for short-range interactions, $U_{reac}(r)$ is the Morse potential, and $f_{c1}(r)$, $f_{c2}(r)$ are the cutoff functions. The purely repulsive short-range term $U_{core}(r)$ was based on the Thomas-Fermi model of an atom, as parameterized by Molière[2],

$$U_{core}(r) = (A/r)\left(0.35\exp(-0.3r/a_s) + 0.55\exp(-1.2r/a_s) + 0.1\exp(-6.0r/a_s)\right) \tag{2}$$

Here, A/r is the Coulomb repulsion between a pair of bare nuclei, while a_s is the Firsov screening length[3]

$$a_s = 0.88534 a_{\text{Bohr}} \left(Z_1^{1/2} + Z_2^{1/2}\right)^{-2/3} \tag{3}$$

which is expressed as a function of the atomic numbers Z_1 and Z_2 of the two atoms, and the Bohr distance a_{Bohr}=0.529 Å.

The reactive part $U_{reac}(r)$ was represented by the Morse potential:

$$U_{reac} = D_e\left[\exp\left(-2\alpha(r_{ij} - r_e)\right) - 2\exp\left(-\alpha(r_{ij} - r_e)\right)\right] \tag{4}$$

where D_e is the potential well depth, α is related to the force constant of the bond, and r_e is the equilibrium interatomic distance. The parameters of the Morse potential were obtained using the GAMESS program[4]. The cutoff functions f_{c1} and f_{c2} were given by

$$f_{c1}(r) = f_c\left(r, D_{\min 1}, D_{\max 1}\right), \tag{5}$$

$$f_{c2}(r) = f_c\left(r, D_{\min 2}, D_{\max 2}\right), \tag{6}$$

$$f_c\left(r, D_{\min}, D_{\max}\right) = \begin{cases} 1, & r \le D_{\min} \\ \left[1+\cos\left(\pi\left(r-D_{\min}\right)/\left(D_{\max}-D_{\min}\right)\right)\right]/2, & D_{\min} < r < D_{\max} \\ 0, & r \ge D_{\max} \end{cases} \quad (7)$$

In eqn. 1, f_{c1} is used for smooth switching between U_{reac} and U_{core}, while f_{c2} ensures that the total potential is truncated beyond the range of chemical interactions. The values of the parameters used in U_{tot} are given in Table I. Due to inapplicability of the pair potential to multi-body interactions at the surface, the reactive non-zero term was only employed for the F-F pair. Morse parameters obtained for the F_2 molecule from DFT using B3LYP density functional and the 6-311G* basis set were D_e=-1.50 eV, r_e=1.405 Å, and α=3.37 Å^{-1}. The absolute energy of an F atom, as well as absolute energy, geometry, and energy Hessian of an F_2 molecule are listed in Table II.

3. Simulation

Primary F atoms were launched at the target at 45° with respect to the surface normal at random incident points and with random azimuthal directions. The classical equations of motion were integrated using the Verlet algorithm. The simulations were stopped when all of the atoms with the kinetic energy higher than a certain threshold have left the vicinity of the target. All outgoing F_2 molecules were recorded based on the criterion $E_{tot}^{F_2} = K_{tot}^{F_2} + U_{tot}^{F_2} < 0$, where $K_{tot}^{F_2}$ is the kinetic energy of the molecule in its center of mass system, and $U_{tot}^{F_2}$ is its potential energy. After each impact, the positions of the atoms in the target were restored to their initial values. The energy spectra with total kinetic energies of outgoing F_2 molecules in the laboratory reference frame were recorded. All spectra were obtained with 10^7 primary impacts.

References

(1) A. Migani, F. Illas, *J. Phys. Chem. B* **110**, 11894 (2006).

(2) G. Molière, *Z. Naturforsch*. **2a**, 133 (1947).

(3) O.B. Firsov, *Sov. Phys. JETP* **5**, 1192 (1957).

(4) M.W. Schmidt, K.K Baldridge, J.A. Boatz, S.T. Elbert, M.S. Gordon, J.H. Jensen, S. Koseki, N. Matsunaga, K.A. Nguyen, S.J. Su, T.L. Windus, M. Dupuis, J.A. Montgomery, *J. Comput. Chem.* **14**, 1347 (1993).

Table I. Values of D_{min} and D_{max} parameters used in the cutoff functions

	D_{min1}, Å	D_{max1}, Å	D_{min2}, Å	D_{max2}, Å
F-F	0.3	0.9	1.9	2.4
F-Ag	0.3	0.9	N/A	N/A
Ag-Ag	0.3	0.9	N/A	N/A

Table II. Absolute energies and geometry of an F atom and F_2 molecule obtained with GAMESS using B3LYP density functional and the 6-311G* basis set

	E_{tot}, Hartrees	r_e, Bohr	Energy Hessian, Hartrees/Bohr^2
F	-99.7208	N/A	N/A
F_2	-199.4968	2.6549	0.3511